Art. XI. – *On the Conductivity of a Solution of Copper*

Sulphate.

(With Plates XV and XVI.)

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The following observations were made with the intention of examining, under various conditions, the conductivity of a salt solution, which is of some importance at present, owing to the attention being paid to solutions now by Ostwald, van't Hoff, and others. I chose copper sulphate ($Cu\,SO_4 + 5\,H_2O$) to work with, as that was the most convenient. It is plentiful and easily purified, and copper is a convenient metal to use for making the electrodes.

All the methods of measuring electrolyte resistance by the ordinary Wheatstone bridge and galvanometer are more or less unsatisfactory, the only satisfactory method being that suggested by Kohlrausch, namely, of using rapidly alternating currents and a telephone, instead of steady currents and a galvanometer. The alternate current may be produced by a small dynamo, but much more conveniently by an induction coil maintained by a few cells. A small coil is preferable to a large one, as the statical charge on the electrodes, especially if they be small, is liable to introduce a serious error, besides which is the annoyance of receiving shocks on touching exposed parts of the circuit, if one works with such high E.M.F.'s as are produced in a large coil. The coil I used, when maintained by four freshly charged Grove cells, gave a spark of rather more than a centimetre, but I generally used a much weaker primary current. A slide wire bridge is generally recommended, but I found a resistance box more sensitive and more convenient. The greatest sensitiveness I ever obtained was about 1 in 1500, that being with a resistance of 1500 ohms. The distribution of resistances which is most advantageous in the arms of the ordinary Wheatstone bridge is by no means the best in Kohlrausch's arrangement. In the former, it is

necessary to arrange the arms so that when the resistances are balanced, the maximum current shall pass through the galvanometer, and generally the variable arm can be so arranged that there is no perceptible deflection of the needle. But in Kohlrausch's method, one cannot get complete silence in the telephones, and a variation of say 1 per cent. is more noticeable in a feeble sound than in a loud one, and so (unless the currents be very weak) the arms have to be arranged to send the minimum current through the telephones. This method also differs from the ordinary in its inability to measure with accuracy low resistances, less than 10 ohms, neither can it measure very high resistances more than 50,000 ohms, although, with the box I had, I could otherwise have measured 1,000,000 ohms. Where one tries to measure these high or low resistances, it is found that when the resistances are approximately balanced, it takes a considerable alteration, say 5 per cent. in the variable arm, to produce any perceptible change in the sound in the telephone, and when the change is produced, it is not so much a change in intensity as in quality—it almost seems like an alteration in pitch, though that could not be. Besides overcoming the difficulty introduced by polarisation, there is an enormous advantage in Kohlrausch's method in the way of rapidity. Making an observation is the matter of seconds, instead of minutes.

The cell I used to examine the effect of change of temperature on conductivity was a glass tube (see Fig. 1), about 20 cm. in length, and 1 cm. in diameter, slightly bent. The ends of this fitted into two flat copper cups, with holes in the sides, fitted with slightly conical necks. These cups were about 7 cm. × 5 cm. × 2 cm. The space between the glass and the copper necks was tightly packed with loose hemp, and formed a perfectly water-tight joint. Wires soldered to the cups gave a means of connection, the cups, or rather their interior being the electrodes, the surfaces exposed to the solution being about 80 square cm. The cups were closed at the tops by blocks of indiarubber cut to fit. I had some difficulty, however, in making these quite water-tight, and tried several methods of stopping up the cracks. It was easy enough to stop them at ordinary temperatures, but the difficulty was to find some cement that did not soften at 100° C. Sealing-wax and putty were among the things I tried, but neither remained water-tight at 100° C. A solution of indiarubber in naptha was finally

tried, and with complete success, and I found the whole cell now water-tight even under considerable hydrostatic pressure. Glass tubes were passed through the indiarubber blocks, and Liebig condensers were attached to these by pieces of indiarubber tubing. The inner tubes of the condensers were closed at the top by corks. The condensers were held vertically by clamps, and the cell was thus suspended. It was immersed in oil to a depth of about 6 cm. (dotted line in figure). I had to keep it hung, as my bath was copper. I tested the insulation of the oil, and could get no current through a very slight thickness of it. When heating a solution, air bubbles began to form at about 75° C. The bending of the tube was to allow the escape of these when they became large enough, as well as to allow the steam to escape more readily when the temperature rose to boiling point. The condensers were, of course, intended to keep the solution at a constant strength. Observations of the resistance above 70° were made after the solution had been well boiled, so that there were no air bubbles to increase the resistance of the system.

To observe the temperature, I took a glass tube of the same section and thickness as that of the cell, and corking one end, I partially filled it with the same solution as that with which I was working, and putting the thermometer into this, I put the tube in a slanting position in the bath. Under these conditions, I considered that the temperature of the solution in the second tube ought not to differ much from the temperature of the solution in the cell. For extra security, however, I always kept the temperature within a degree or two for several minutes, and within $\frac{1}{5}$ degree for about half a minute before taking a reading of the resistance. The salt I used was ordinary commercial copper sulphate which I purified by making strong super-saturated solutions in distilled water, and taking the crystals which were deposited before the solution became cold. I obtained the strength of each solution by weighing the amounts of salt and water in it, and checked the results by taking the density with hydrostatic balance, using a glass sinker, and then comparing these values with a series previously obtained and plotted.

I made a very great number of observations altogether, but finally have drawn my conclusions from eight sets, which were the last made, and on which I spent more time and pains than on the others. In the results which follow,

T is the temperature centigrade, R the observed resistance of the system in legal ohms, and k is the conductivity, *i.e.*, the reciprocal of the specific resistance. Taking s as the specific resistance $r = \frac{l\,s}{\pi\,r^2}$, where r is the mean radius, and l is the length increased by $\cdot 8\,r$ at each end, $\frac{l}{\pi\,r^2}$ is a constant for the instrument determined by measurement once for all. Thus $k = \frac{l}{\pi\,r^2} \cdot \frac{1}{k}$ and $\log k = \log \frac{l}{R} - \log R = 1\cdot2540 - \log R$, so that the calculation of k from the observed resistances is very simple. The following tables show all the observations used from which I calculated my results :—

	5·98 %			25·70 %			9·24 %	
T	R	k	T	R	k	T	R	k
17	1155	·01554	18	409	·0439	17	852	·0211
31	887	2025	30	320	·0561	30	669	268
41	769	2335	42	260	·0690	42	558	322
50	679	2645	54·6	220	·0816	55	482	372
60	629	2855	70	195	·0920	70	435	413
70	589	305	81	181	·0992	82	630	281
99	537	3343	88	174·5	·1022	70	433	414
97	537·5	334	98	165·0	·1088	95	409	439
94	540	332	96	167·0	·1075	99	404	444
89	548	328	92	170·0	·1056	91	407	441
80	556	323	88	173·0	·1038	88	413	435
70	581	309	81	179·2	·1002	80	420	427
						85	414	434

	3·34 %			2·51 %			1·258 %	
T	R	k	T	R	k	T	R	k
18·9	1800	·00997	18·3	2290	·00784	15·8	4030	·00445
31	1459	·01230	30	1837	·00977	35·2	2800	641
45	1225	1465	40	1598	·01123	52	2350	764
60	1066	1684	50	1440	·01246	65	2120	847
70	999	1796	60	1335	1344	80	1990	902
80	962	1866	70	1266	1418	. . . .		. . . .
100	928	1934	80	1218	1474	80	1957	917
99·7	929	1932	97	1174	1529	90	1915	937
98·5	930	1930	94	1175	1528	94	1925	932
95	932	1926	90	1182	1519	97	1915	937
92	933	1924	85	1192	1506	100	1901	944
90	935	1920	80	1212	1481	97	1903	943
87	940	1909				94	1901	944
85	943	1903						
80	957	1875						

	·597 %			·262 %	
T	R	k	T	R	k
59	3270	·00549	99	6270	·00286
97	3250	552	96·5	6260	287
95	3235	555	94	6260	287
93	3230	556	91	6280	286
89	3230	556	86·5	6330	283
87	3235	555	80·5	6430	279
84	3250	552	70·3	6740	266
82	3260	550	18	13850	1296
80	3280	547	30·5	10870	1651
70	3406	528	45	8900	2017
16·3	6650	270	60	7550	2377
30·2	5060	355	70	7000	2564
46	4130	435	80	6550	2740
69	3650	492	70	6900	2601
70	3380	531			

I had now to find, first, the law of variation of conductivity with temperature, and second, its variation with strength of solution. In working out the former, I took 20° C. as my standard, and in what follows, t is the excess of temperature over 20°. I found that each set of observations was given within the limits of errors of observation by the formula $k_t = k_{20} (1 + a\,t - \beta\,t^2)\, k_t$ and k_{20} being the conductivities at $20° + t°$ C. and 20° C. respectively. To determine a and β as accurately as possible, I worked it out in each case by the "method of least squares," working from the conductivities at 20, 30, 40, 50, 60, 70, 80, 90, and 100° C. found by interpolation from the results given above.

The values I found are shown in the following table :—

n (Solution Concentration).	k_{20}	a	β
25·7 %	·0458	·0254	·000100
9·24	·0224	·0237	140
5·98	·0165	243	144
3·34	·0102	211	125
2·51	·00808	221	136
1·26	·00482	231	138
·597	·00293	215	115
·262	·00135	220	69

From this table it will be seen that a and β are fairly constant for all solutions, though perhaps a increases slightly with the concentration. The errors in β are too great and too irregular to indicate any law of variation. Assuming then that a and β are constant, we find the mean values are, $a = \cdot0229$; $\beta = \cdot000121$. In a the probable error of the result is $\cdot00054$, or a little less than $2\frac{1}{2}$ per cent. of the whole. Although the values of a and β thus found give the conductivity with fair accuracy, yet they fail in one particular. It will be seen on examining the results in the case of the last two solutions, that there is a temperature of maximum conductivity somewhere between 90 and $100°$ C. In previous experiments, however, I got maxima between 90 and $100°$, with solutions of 3 and 6 per cent., it being very marked in the latter case. It is possible that there may be a maximum in every case, but generally above $100°$ C., and that its position may vary considerably with very small impurities in the solution, though I do not know what impurity I could have introduced in the one case and not in the other, as in each case I used water distilled in the same way, and salt from the same vessel.

I should remark that, in calculating a and β in the case of the solutions that have a maximum under $100°$, I only used the results between $20°$ and $80°$.

It now remained to determine the law connecting conductivity and concentration (k and n). After trying various formulæ and plotting several functions of k and n, I at last suspected that k varied as some power of n, and on taking logarithms and plotting them, I found the resulting curve very nearly a straight line, the deviations from it being such as might arise from errors of observation. Putting $k = a\,n^{b}$, we have $\log k = \log a + b \log n$. This is a very simple form to work out by "least squares," and I found the constants were $a = \cdot00403$, $b = \cdot766$, the average error being $3\cdot4$ per cent. The general expression for the conductivity thus becomes $k = \cdot00403 \times n^{\cdot766}\,(1 + \cdot0229\,t - \cdot000121\,t^{2})$. The curves I, II, and III show the relations between the conductivity and temperature for three different solutions, and may be taken as typical. The curves themselves are plotted from the mean values of the temperature coefficients, and the crosses show the actual observations. As I remarked previously, the coefficients are probably some function of the concentration, but my results are not accurate enough to determine it. Curve IV shows the logarithms of

the different values of the conductivity and concentration; as before, the curve showing the mean calculated values, and the crosses the observed values.

The following table gives the conductivities for several concentrations and temperatures, and may be useful for reference :—

Temp.	Concentration.						
	·1 %	·5 %	1 %	5 %	10 %	20 %	30 %
20	·000690	·00237	·00403	·0138	·0235	·0398	·0543
30	·000840	403	490	168	286	484	661
40	·000975	335	569	195	332	562	767
50	·001090	374	635	218	371	628	857
60	·00119	408	693	238	405	685	936
70	·00127	436	741	254	433	733	1000
80	·00133	459	780	267	455	771	1050
90					472	800	1090
100					483	819	1120

DESCRIPTION OF PLATES XV AND XVI.

FIG. 1.—*a*, glass tube; *b b*, copper cups; *c c*, indiarubber blocks; *d*, hemp packing; *e e*, Liebig condensers; *f*, level of solution in cell; *g*, level of bath in which cell is immersed.

FIG. 2.—Curves I, II, III, showing agreement between mean value of temperature coefficients, and values in typical cases. Abscissæ represent temperature centigrade; ordinates, conductivity.

FIG. 3.—Curve IV, showing that the connection between the logarithms of the concentration and conductivity is linear, and consequently, that the conductivity varies as a power of the concentration. Abscissæ, logarithms of conductivity; ordinates, logarithms of concentration.